Advanced Composite Coatings for Industries of the Future

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<u>Partners</u>

Dr. Eric Minford; Air Products and Chemicals, Inc.
Dr. Jeff Price; Solar Turbines
Dr. Walt Sherwood; Starfire Systems, Inc.

5-year Project 2001-2006, $1.35M

UW $75K/yr, UCF $50K/yr, PNNL $175K/yr.

Project Objectives

- Research and develop low-cost ceramic coatings for prevention of high-temperature corrosion of metals and ceramics in industrial uses, such as chemical processing and power generation.
- Coatings will provide protection at 700°C to 1000°C from corrosion due to oxidation, carburization, coking, and metal dusting.

Program Structure

- Primary coating development and research will be performed by PNNL and the University of Washington (Prof. Raj Bordia, Jessica Torrey).
  - ↓ PNNL focus on coating development and initial characterization, corrosion testing and evaluation.
  - ↓ UW focus on mechanical properties, evaluation of filler materials, and constrained sintering models.
- Primary coating characterization will be performed by University of Central Florida's Materials Characterization facility (MCF) under the direction of Prof. Lucille Giannuzzi.
- Industrial Partners have been involved in initial project planning and annual meetings of the project team occur.

Technical Approaches

- Another Coating Project?
  - High-temperature ceramic coatings on metals (or ceramics). [T > 1200˚C]
  - Versatile application processes (painting, spraying, spin-on).
  - Tailorable compositions to address: [CTE, hardness, strength, corrosion].
  - Control of coating/substrate interface determined from polymer chemistry.
- Preceramic polymers (polysiloxanes) are used to produce a variety of Si-C-O-N materials which are ideal for low-cost protective coatings, provided that a low cost raw material and processing route can be found.
  - An extremely inexpensive polymer precursor is being used to produce our coatings (cost is a few $/kg).
  - Precursor chemistry is robust for organic attachments that can be used to control final ceramic chemistry.
  - Reactive metal/ceramic fillers can be used to accommodate differential shrinkage, constrained sintering stresses, and thermal expansion.
- Advanced characterization capabilities critical to success of program.

Program Status

- **Four polymers (polysilsesquioxanes) have been tested to explore high ceramic yield systems.**
  - ↓ Excellent ceramic yields, robust range of properties, but too expensive.
- **A low-cost route to polysilsesquioxanes has been developed by Yigal Blum at SRI and incorporated into this project. From $100/lb to $5/lb.**
  - ↓ Two polymers synthesized using this route and filler incorporation is an integral part of polymer chemistry. Currently, we are making filled coatings using this approach.
- **Filler particles have been identified based on theoretical volume expansion and desired coating chemistry.**
  - ↓ Ti, Fe, and Al powders undergo significant expansion. Al powders melt and reduce SiO_2 to Si for subsequent reactions. Al + TiC powders will be explored for displacement reactions during pyrolysis.
  - ↓ SiC powders provide excellent inert filler.
- **Three project meetings have been held at regular intervals at national meetings with participants and partners.**
  - ↓ 2002 and 2003 Annual Meeting of ACerS, 2003 Cocoa Beach Meeting.
- **Six presentations have been made at national meetings, 1 paper is in preparation, and 1 abstract has been accepted for presentation in October.**
  - ↓ 1 at 2002 ACerS Annual Meeting, 3 at 2003 Cocoa Beach Meeting, 2 at 2003 ACerS Annual Meeting.

Brief Background

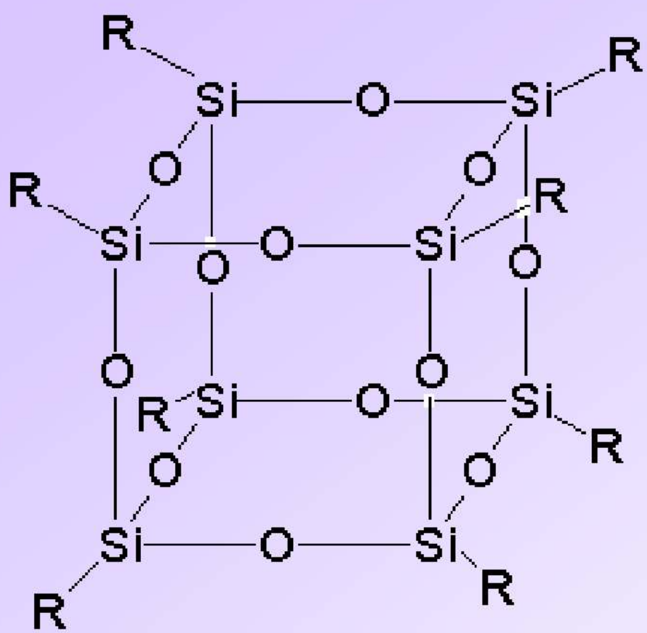
- Polysiloxanes used in producing Si-O-C materials: films, coatings, foams, and matrix materials for composites.
  - Sol-gel process previously (mainly) [Brinker and Scherer].
  - Polysilsesquioxanes form amorphous Si-O-C “black glasses”. Contains “free” carbon but stable up to 1200C in air.
  - Utilized in AFCOP* process. [Greil et al.]
  - Polysilsesquioxanes have excellent ceramic yields and produce flexible, free-standing thin films with appreciable tensile strengths [Y. Abe et al. 1994-present].
  - Homogeneous, smooth, and crack-free films of 0.25 to 0.95 µm thickness produced on polymer, metal, and ceramic substrates by dip coating (1-10 times) [Y. Abe, et al., J. Non-Cryst. Sol. 261 (2000) 39-51].
  - Low-k dielectrics. [T. M. Lu et al.]

*Active Filler COntrolled Pyrolysis (AFCOP)

Polysilsesquioxane Polymers

- Four polysilsesquioxane polymers were selected based on total ceramic yield and functional group chemistry (Gelest, Inc.).
  - ↓ Poly(methylsilsesquioxane) – PMS
  - ↓ Poly(phenylsilsesquioxane) – PPS
  - ↓ Poly(phenylmethylsilsesquioxane)(phenyl:methyl=9:1) – PPMS
  - ↓ Poly(phenylpropylsilsesquioxane) (phenyl:propyl=7:3) – PPPS
- Initial studies performed in Argon, Air, Nitrogen, and Acetylene/N_2 mixture pyrolysis atmospheres.
- Spin coating techniques used to make thin coatings on 316SS substrates.

Polymer Chemistry



A mixed cage/network structure.

Polysilsesquioxanes (from Gelest, Inc.)

Poly(phenylsilsesquioxane), PPS: MW=1,200-1,600
R=100% phenyl

Poly(phenyl-methylsilsesquioxane), PPMS: MW= not known
R=90% phenyl, 10% methyl

Poly(methylsilsesquioxane), PMS: MW=7,000-8,000
R=100% methyl

Poly(phenyl-propylsilsesquioxane), PPPS: MW=1,500-1,800
R=70% phenyl, 30% propyl

R = methyl – CH_3
R = propyl – C_3H_7
R = phenyl – C_6H_5 (attached benzene)

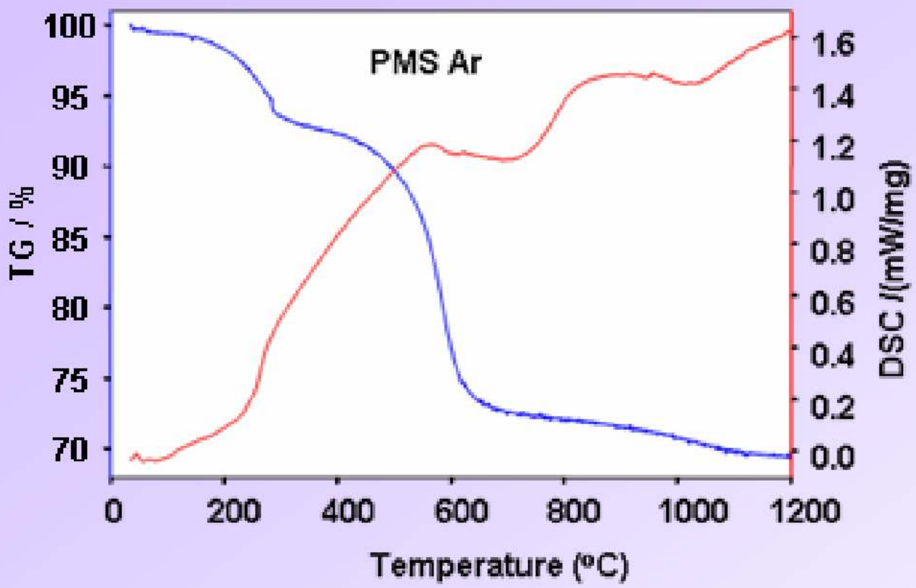
TGA-DTA data

- Polymers were heated in TGA-DTA# up to 1200°C in Air, N_2 and Ar atmospheres.
  - ↓ Compare PMS and PPS data in Air, N_2, and Ar.
  - ↓ Polymers reactive in Air and reaction completed at T < 800°C.
- Ceramic yields* ranged from 45% to 80%.
  - ↓ Lowest yields (highest mass loss) in Air, highest in Ar.

#5°C/min

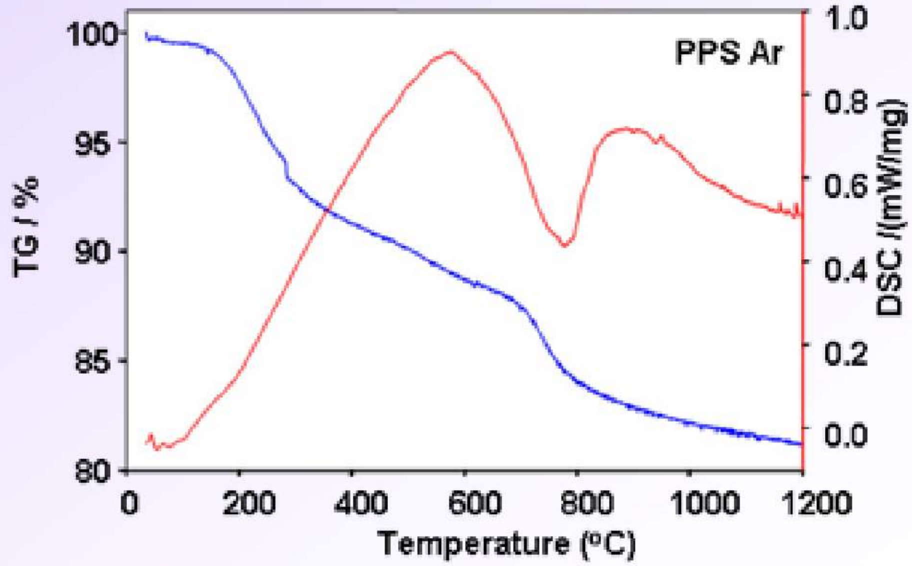
*Defined as percent retained mass after pyrolysis

TGA-DTA Data for PMS and PPS in Ar



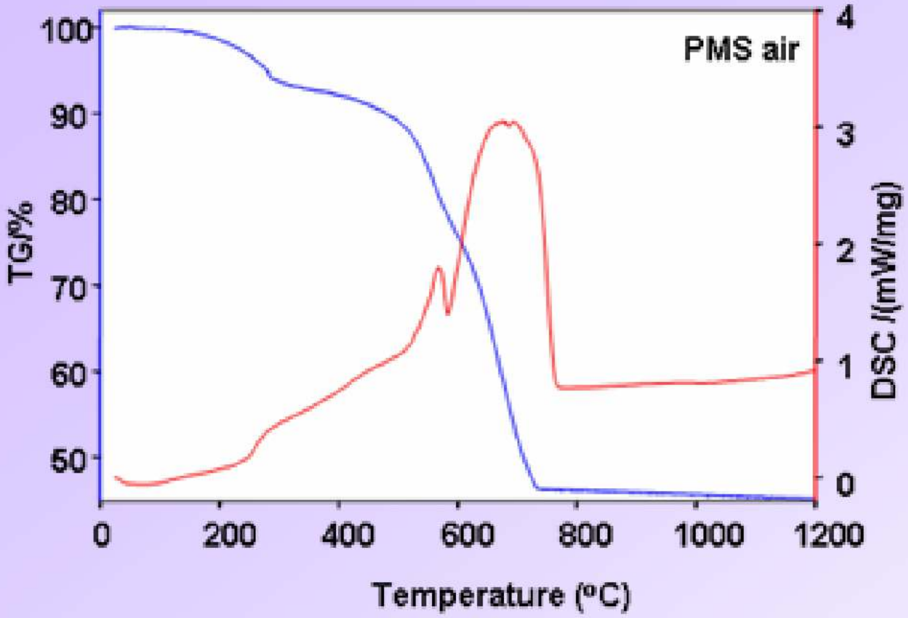
Ceramic yield (%): 69.4

Characterized by multiple reaction peaks at about 500-900˚C. Higher yields.

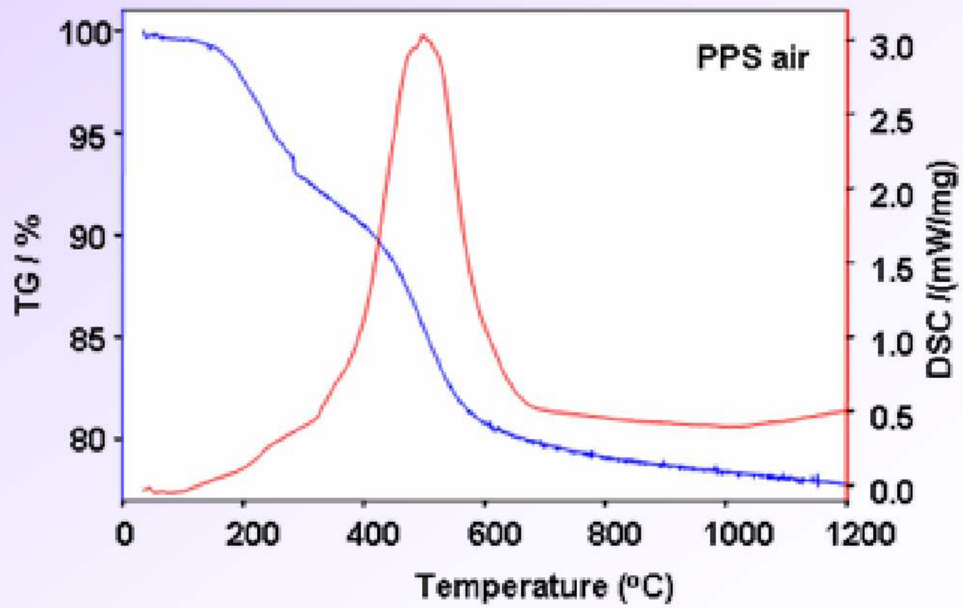


Ceramic yield (%): 81.4

TGA-DTA Data for PMS and PPS in Air



Characterized by a (nearly) single reaction peak at about 500-700˚C.



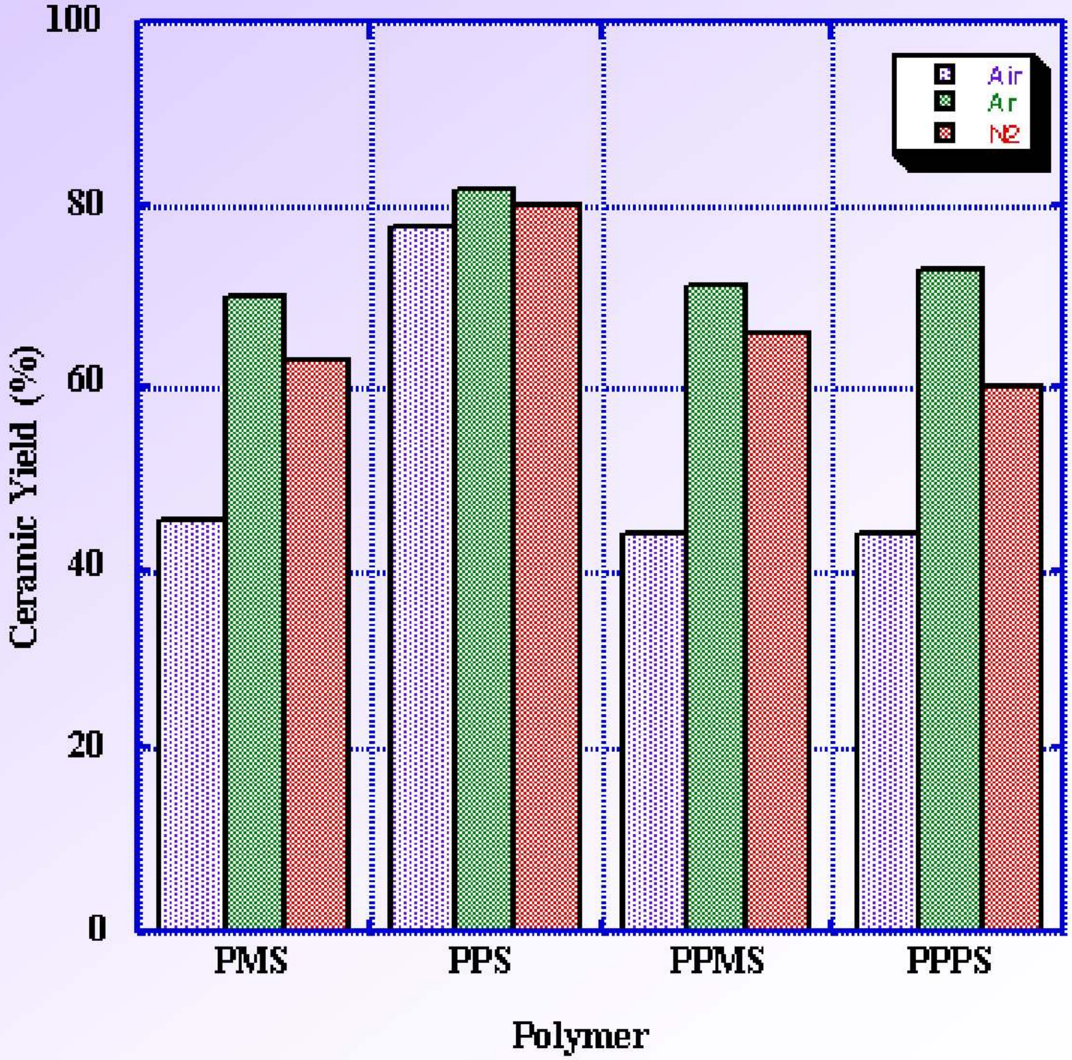
Ceramic yield (%): 45.2

Loss of cage structure and organic group begins to occur at about 250˚C

Ceramic yield (%): 77.8

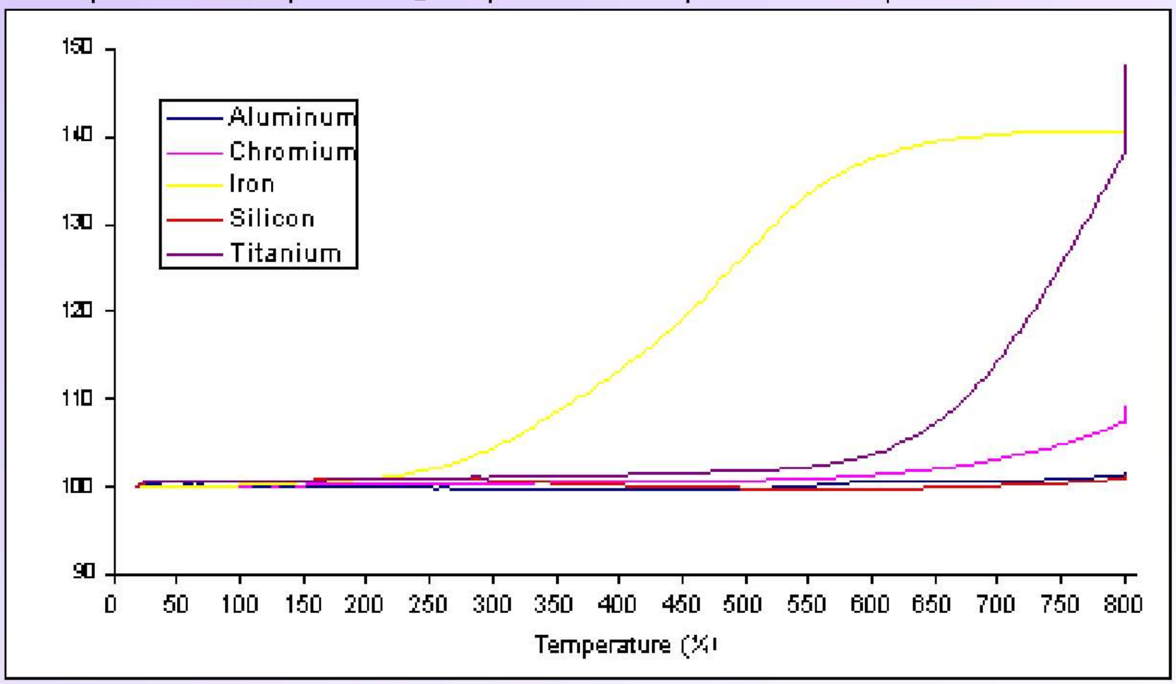
Summary of Polysilsesquioxane Ceramic Yield

Ceramic yield of each polymer plotted as a function of pyrolysis atmosphere after pyrolysis at 1200˚C.



Suitable Expansion Agents

Element	Oxide	KB	expected wt. Gain (%)	actual wt. Gain (%)
Al	Al_2O_3	1.29	89	1.9
Cr	Cr_2O_3	2.01	46	9.6
Fe	Fe_2O_3	2.15	43	40.6
Ti	TiO_2	1.77	67	48.5
Si	SiO_2	1.88	114	1.5



- **Pyrolysis Conditions:**
  - 20-800°C at 1°/min in air
  - Hold 1 hour
- **Particle Size:**
  - Al, Cr, Fe, Si 1-5 μm
  - Ti 7-9 μm
- **As-received powders**

- **Low wt. gain of Si, Al, Cr due to protective oxide layer which prevents diffusion of oxygen**

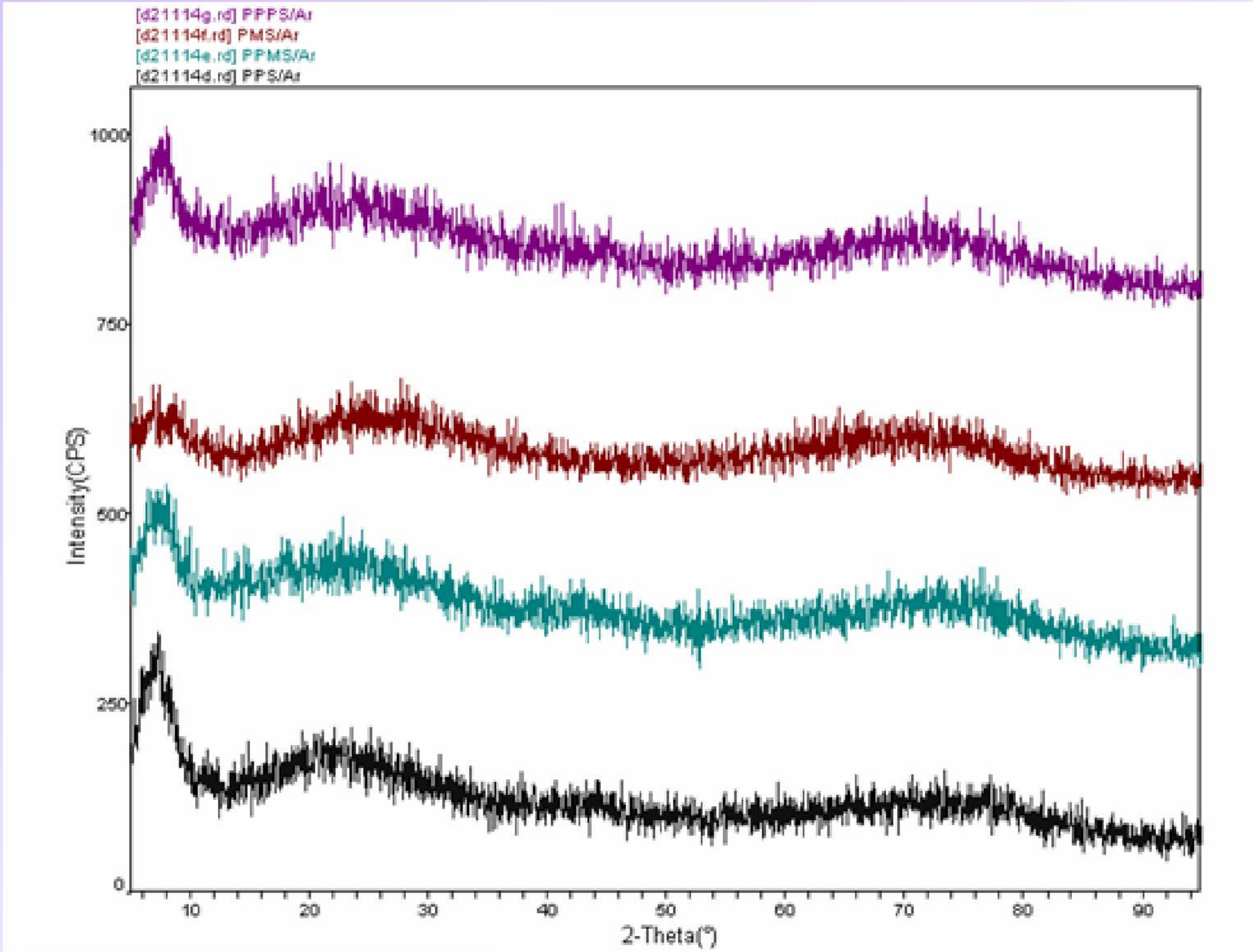
Coating Processing Details

- Polysilsesquioxane polymers were dissolved in toluene or acetone/methanol at 10 wt%.
  - Viscosities were measured using rheometer and set to between 1 and 20 cp by solvent extraction.
- Substrates are 316SS coupons (polished to 1 μm diamond finish).
- Films were applied by spin or dip coating and allowed to air dry overnight.
  - Spin coating at 3000 rpm.
  - Dip coating at 1 cm/min withdrawal rate.
- Pyrolysis performed at 800°C or 700°C in flowing gas for 30 min. in a quartz tube furnace (heating at 5°C/min, cooling at 10°C/min).
  - Argon, Air, N_2, and Acetylene/N_2 mixture

Coating Characterization

- Films were characterized as to structure/composition.
  - Glancing XRD of coated substrates.
    - Films are glassy, no crystalline peaks observed.
  - EDS in JEOL SEM
    - Si-O-C?
  - FIBTEM at UCF
    - Amorphous with nanocrystallites of C?
    - Observe interdiffusion with substrate elements
- Films were characterized for “mechanical” properties.
  - Scribed and Indented
    - Films fracture in brittle fashion

Glancing angle XRD of pyrolysis products in Ar



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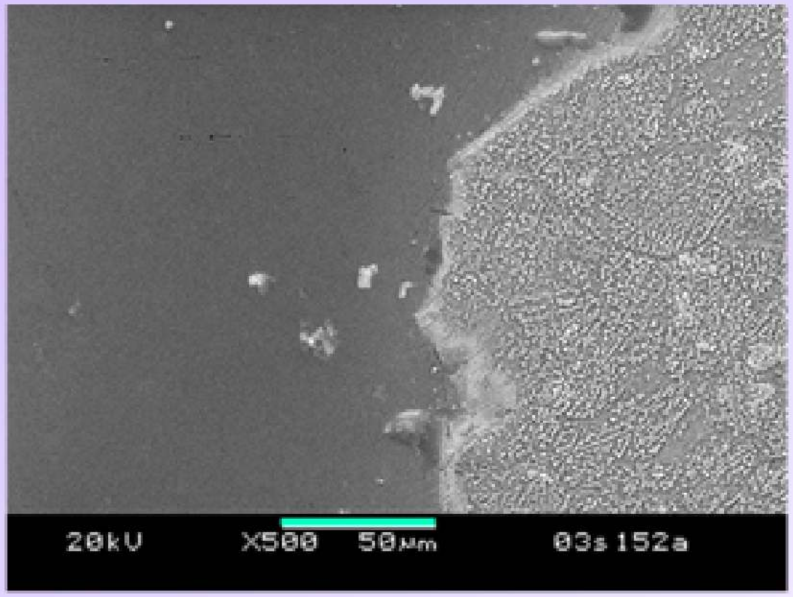
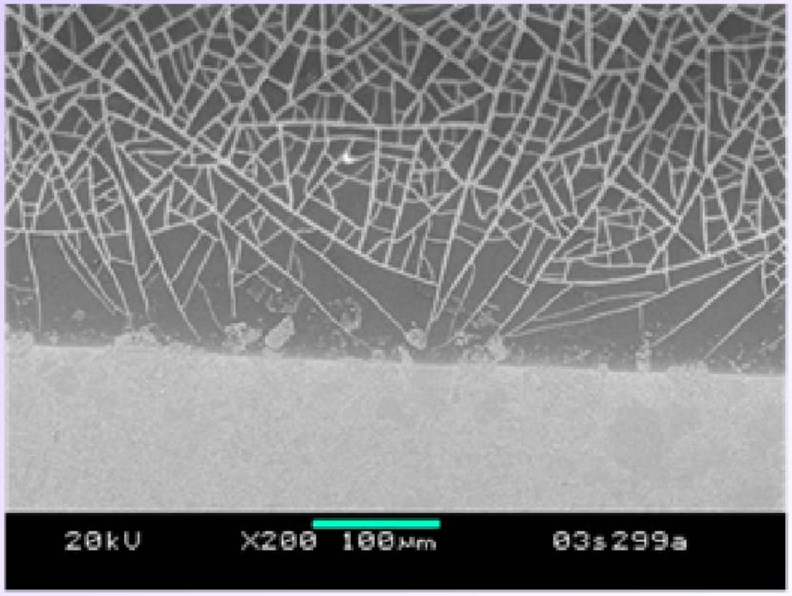
SEM Images of PolyMethyl Films



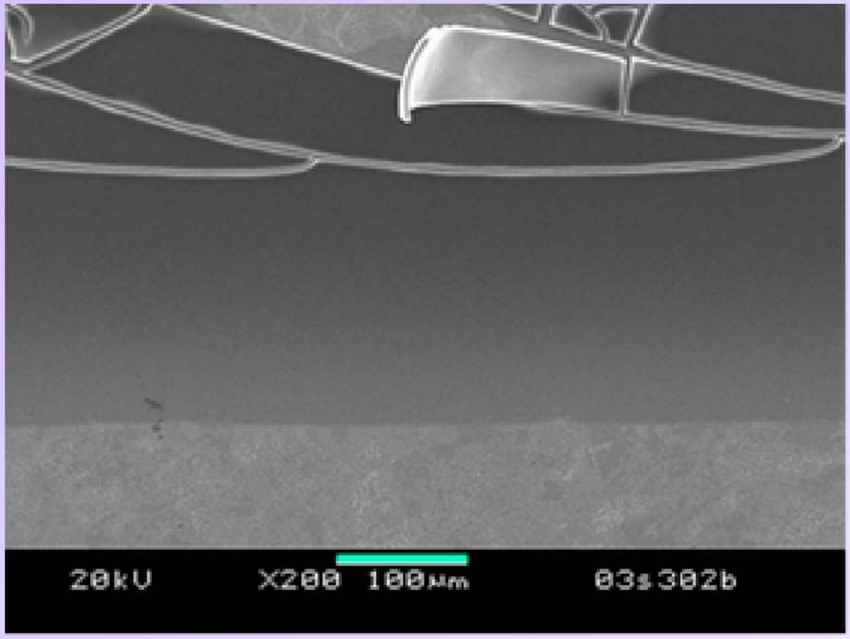
PMS in N_2 at 800°C



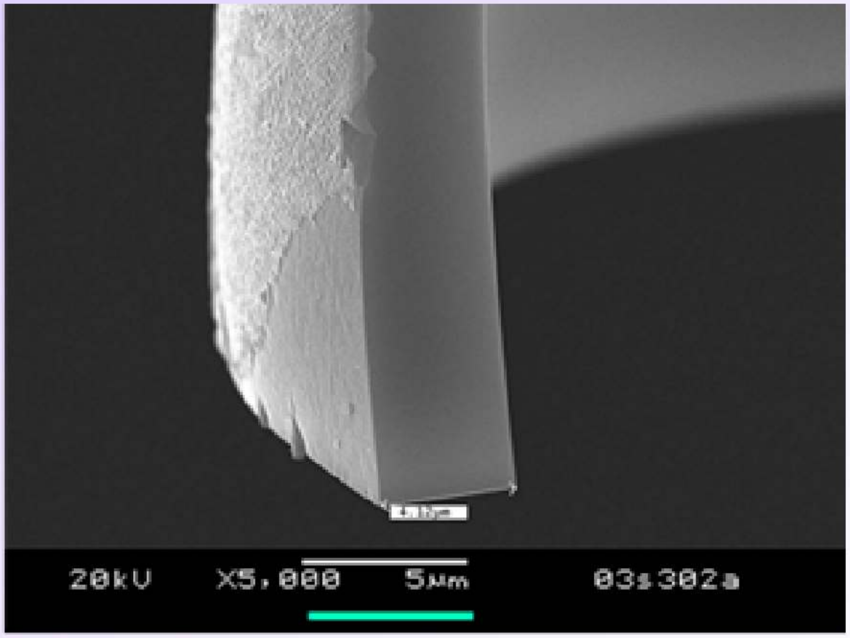
PMS in Air at 700°C

- Films are thin and uniform
  - Observe film cracking in some cases
  - Uniformity controlled by dip coating technique and viscosity
  - Observe protection of underlying substrate

SEM Images of PolyPhenyl Films



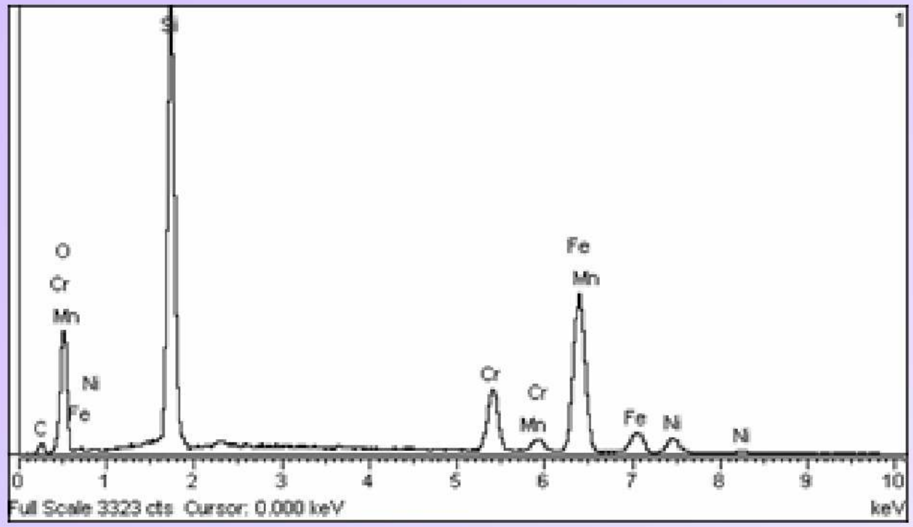
PPS in N_2 at 700°C



PPS in N_2 at 700°C

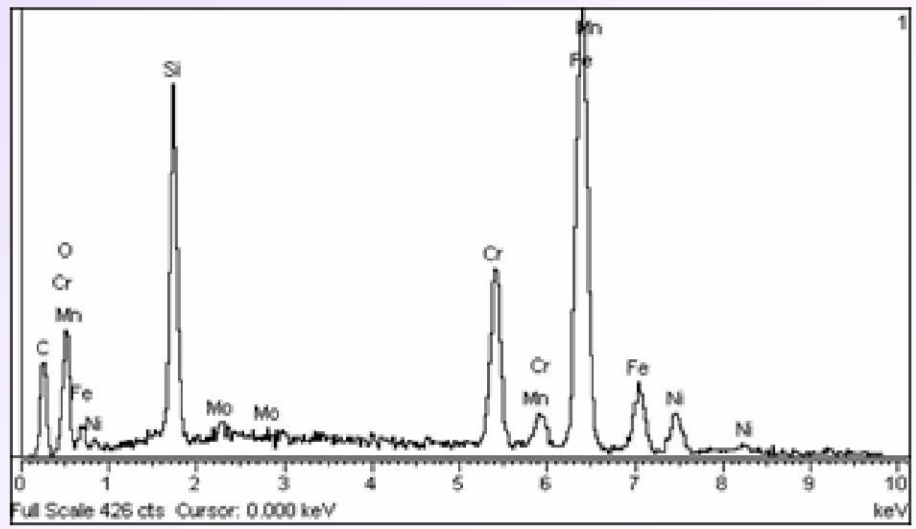
- PPS films are very smooth and uniform
  - Contain more carbon
  - Cracking occurs for t > 3 µm

EDX of Methyl and PhenylMethyl Films



PMS in Ar at 700°C

- Methyl films contain less carbon than other polymer films. Almost SiO_2 in composition, film appears transparent and light brownish in color.
- PhenylMethyl film contains appreciable carbon compared to methyl film, appears opaque and black in color.



PPMS in Ar at 700°C

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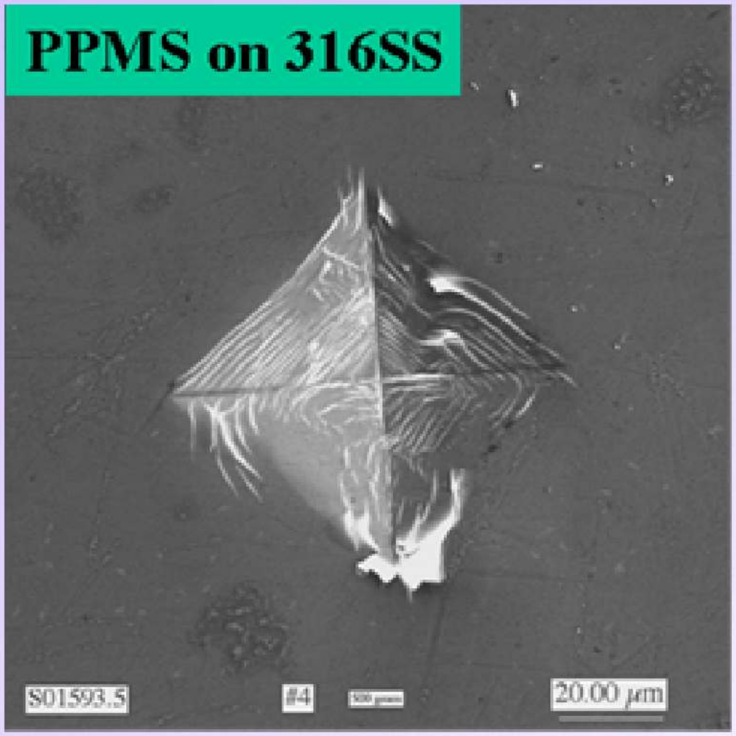
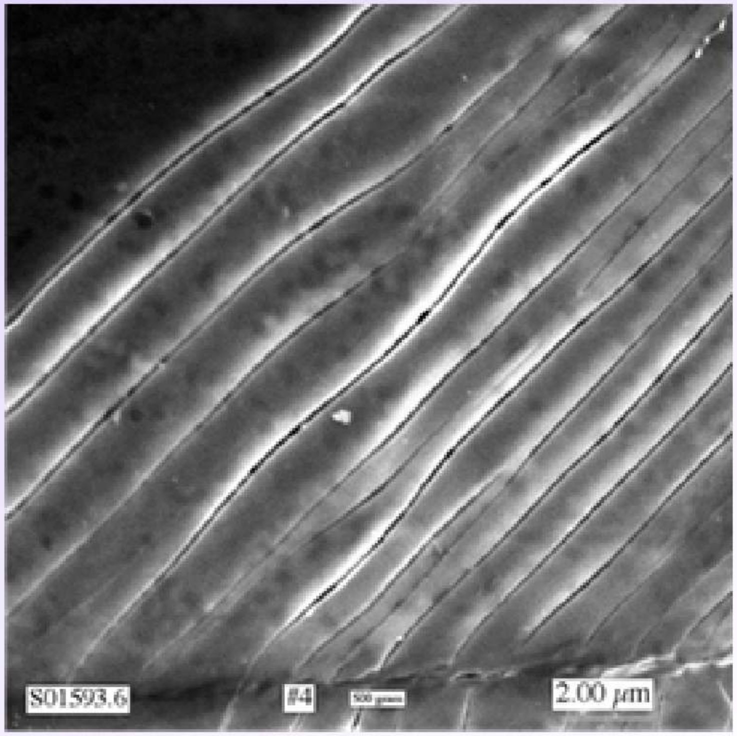
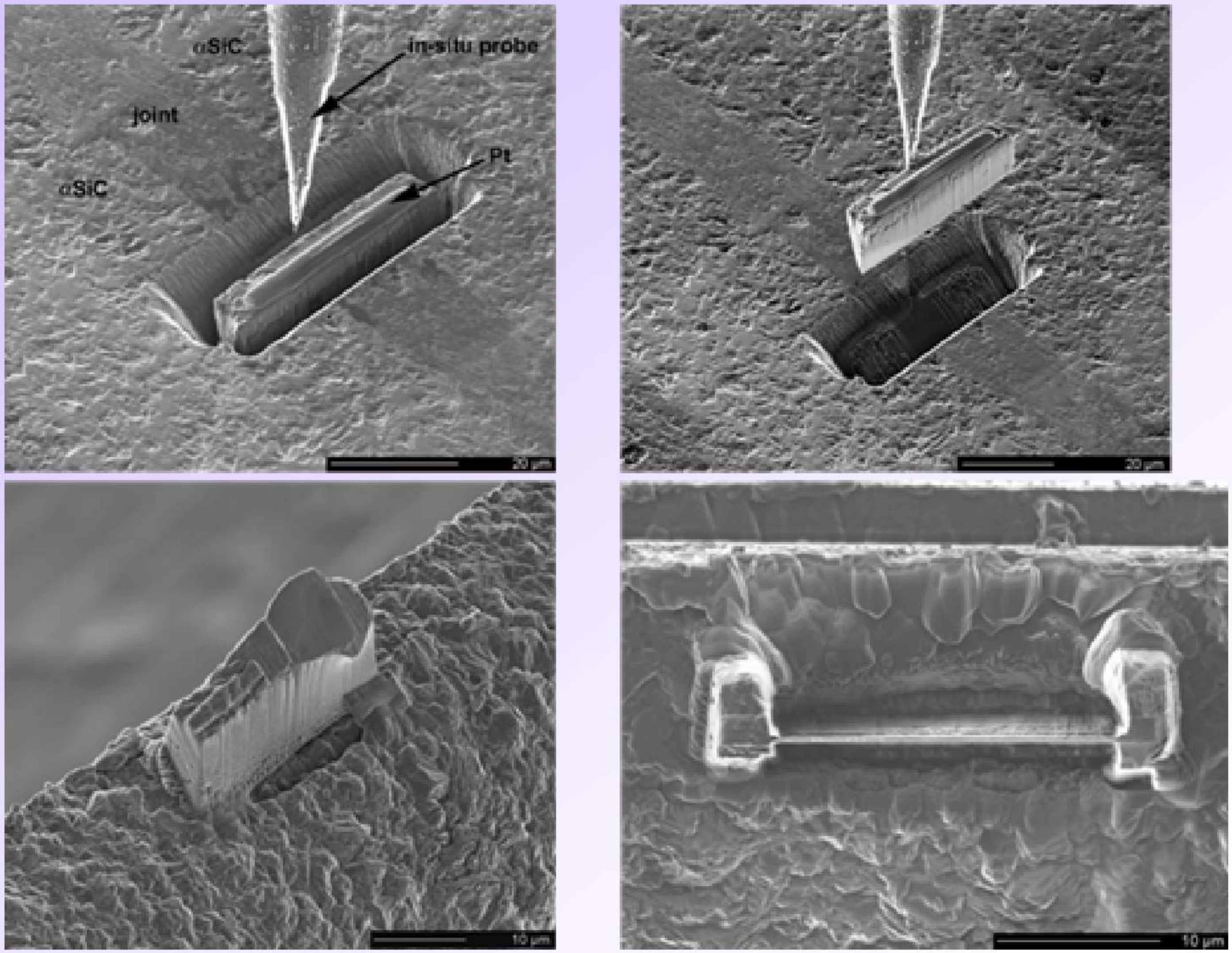
Vickers Indentation of Films



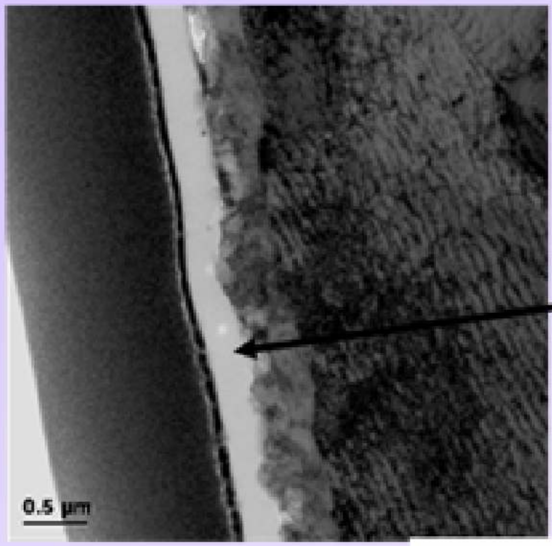


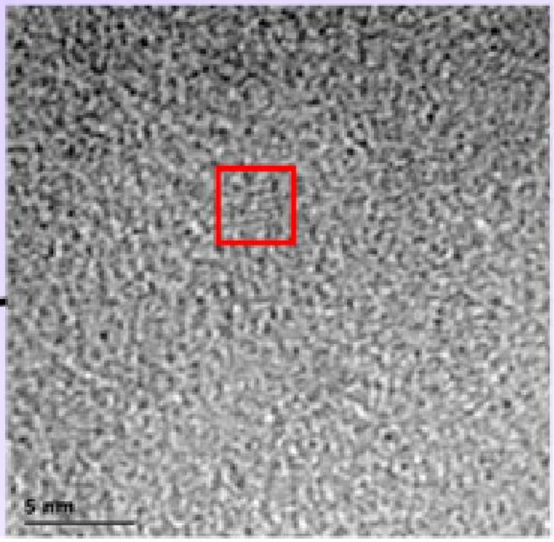
- Brittle coating on compliant substrate. Uniform crack spacing is proportional to film thickness.
- Spalling observed near corners.
- Adhesion appears excellent, however.

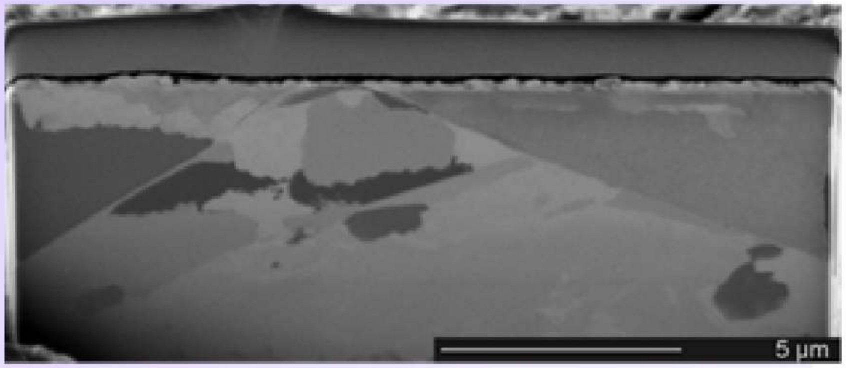
In-situ FIB lift-out

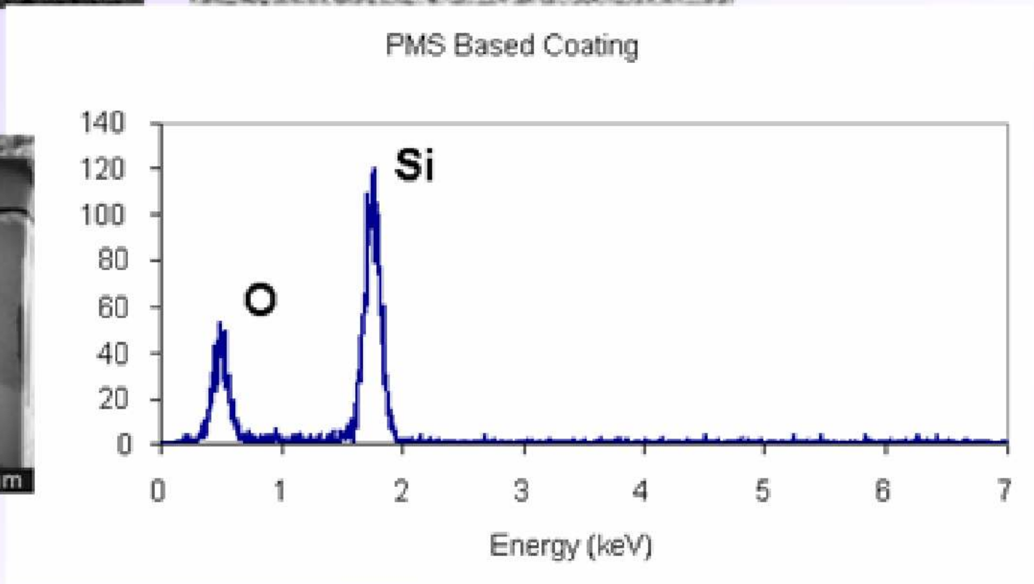


PMS in Ar

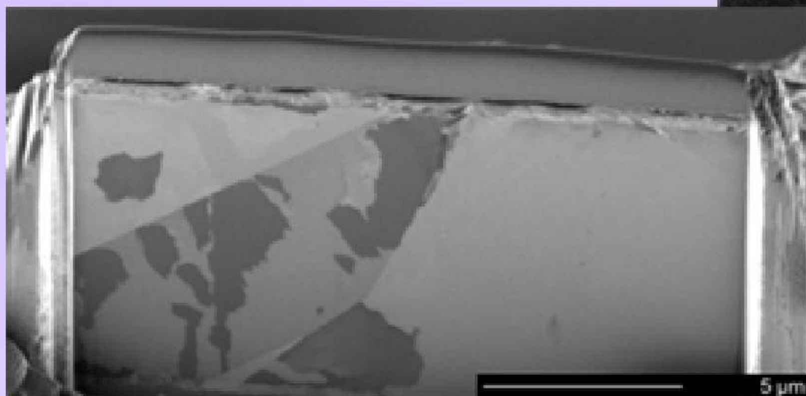

0.5 µm


5 nm

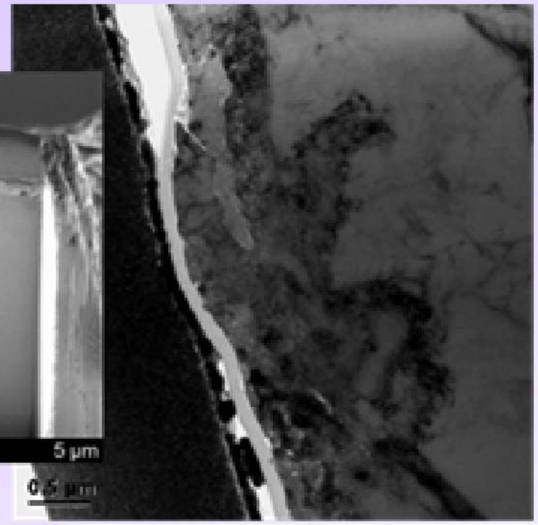

5 µm


PMS Based Coating
140
120
100
80
60
40
20
0
Si
O
0
1
2
3
4
5
6
7
Energy (keV)

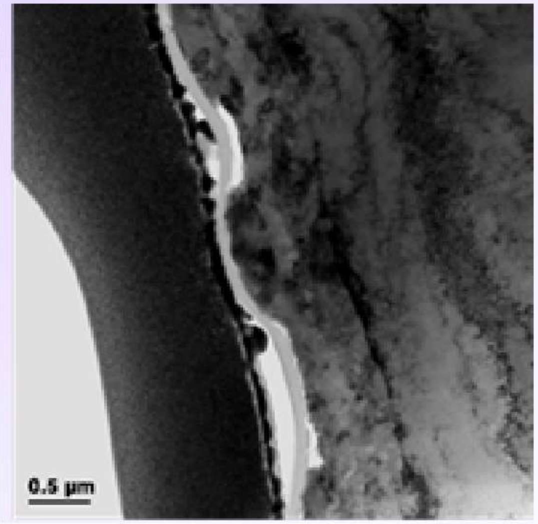
PPS in Ar



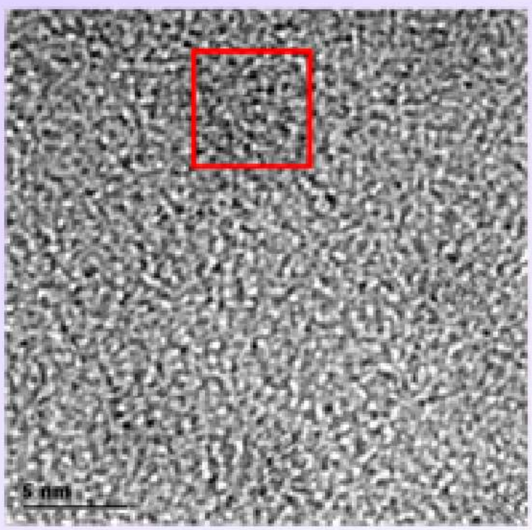
5 µm



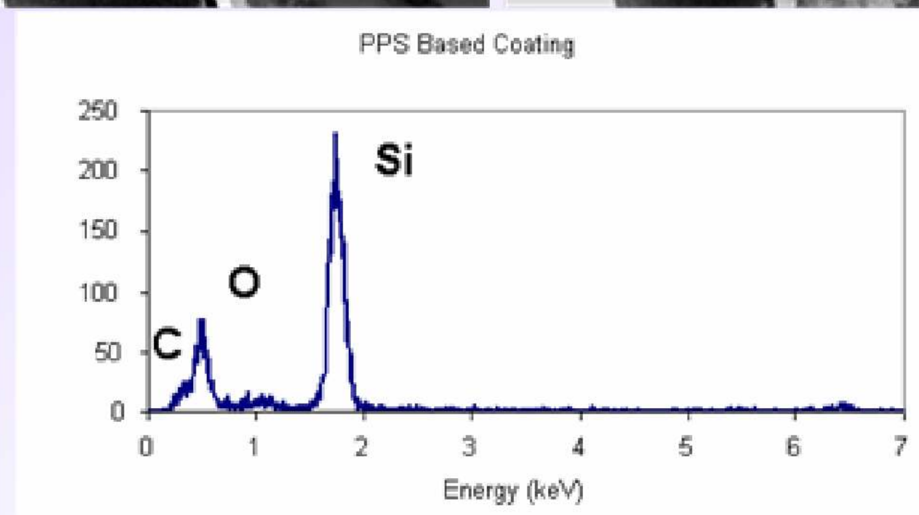
0.5 µm



0.5 µm



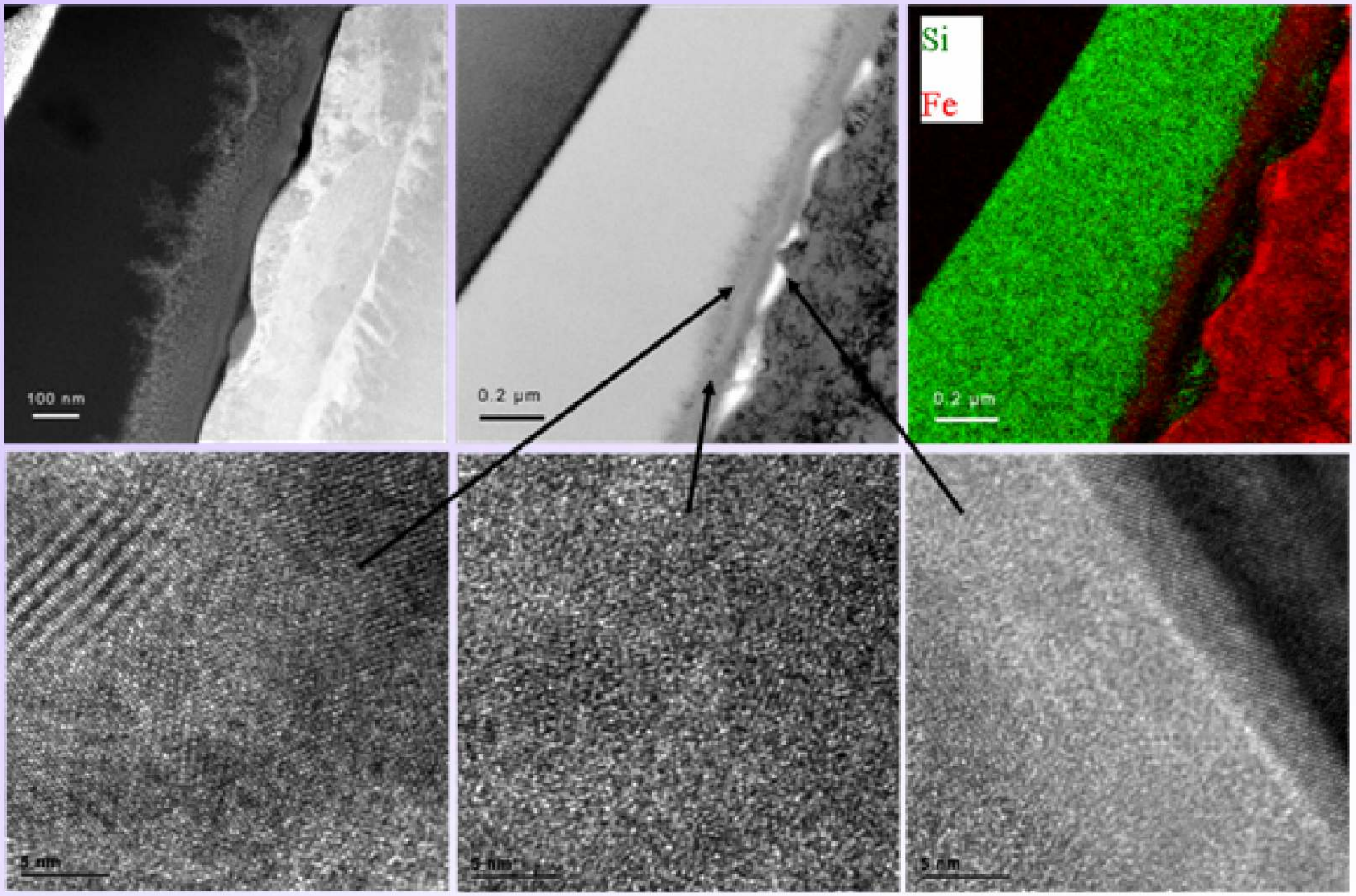
5 nm



PPS Based Coating
250
200
150
100
50
0
0
1
2
3
4
5
6
7
Energy (keV)
Si
O
C

PMS in Air

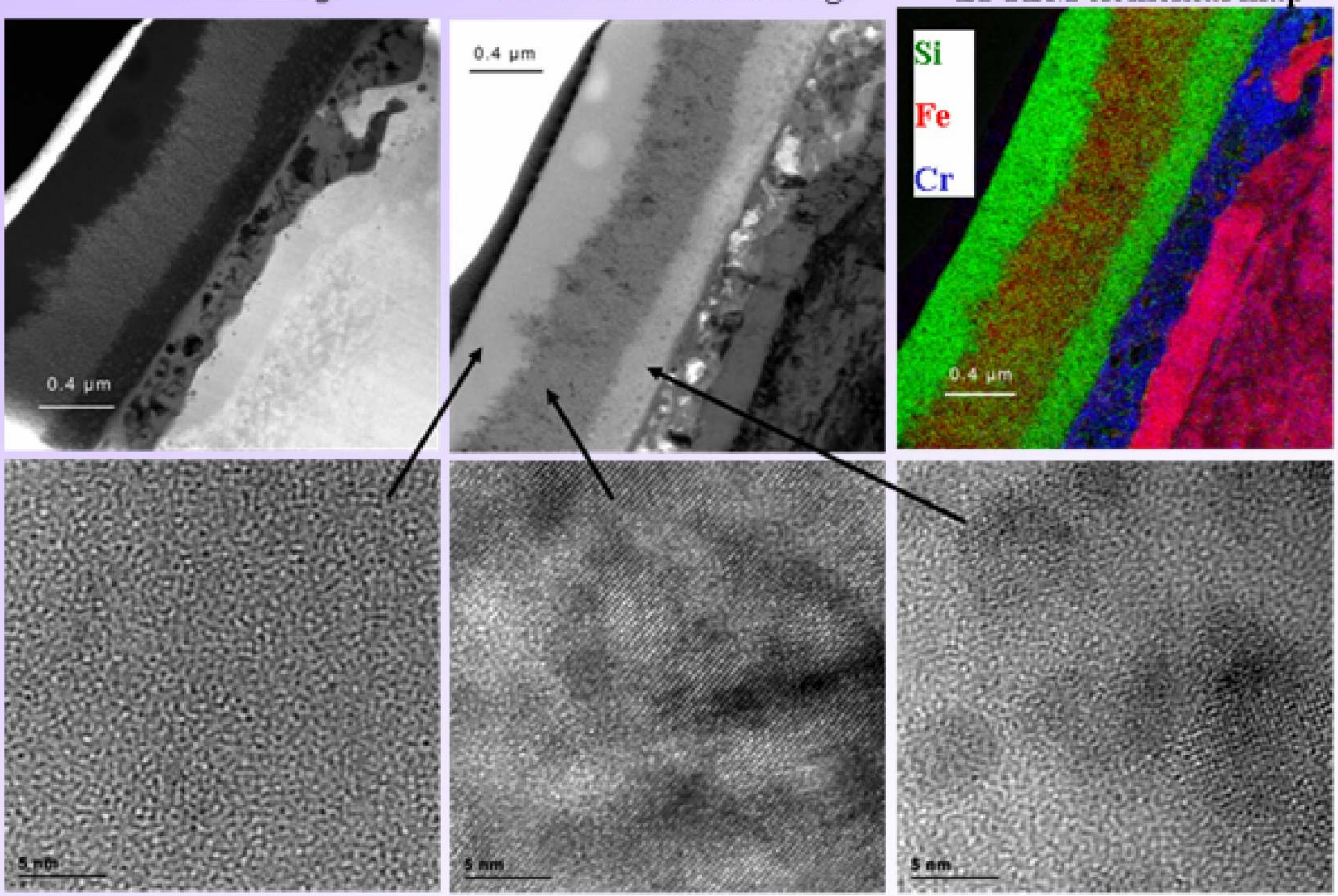
HAADF image | EFTEM zero loss image | EFTEM elemental map



Large ppt in diff zone | small ppt in diff zone | SS/glass interface

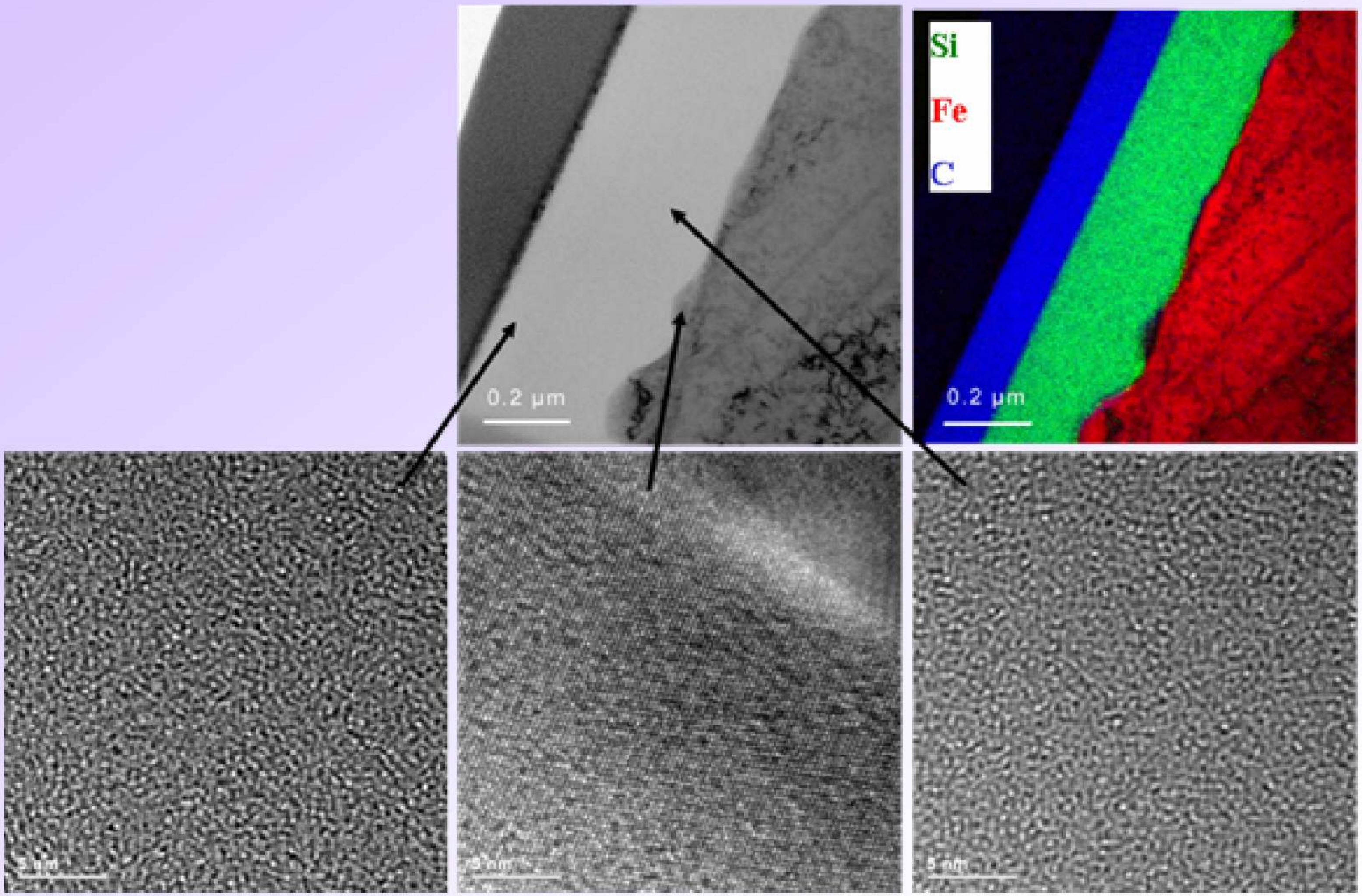
PPS in Air

HAADF image | EFTEM zero loss image | EFTEM elemental map

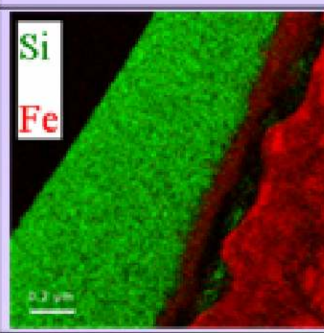
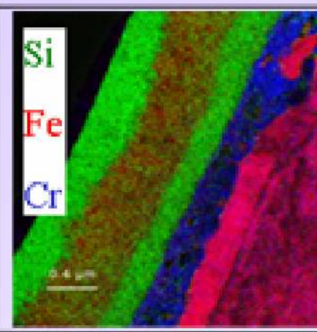
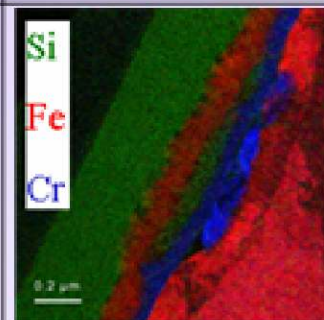
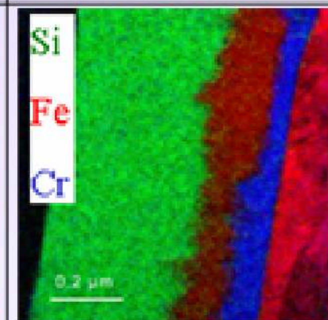
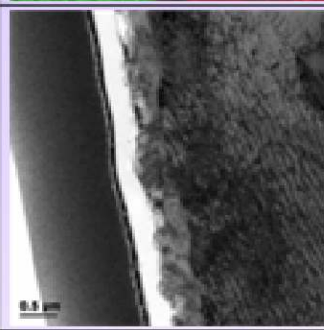
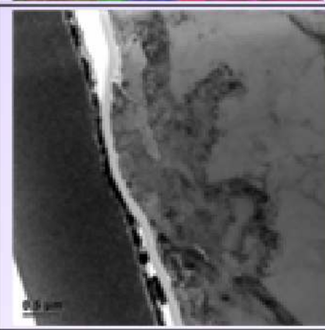
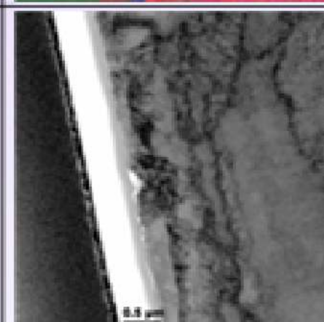
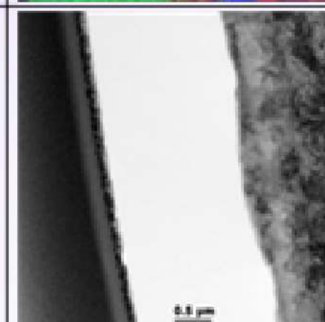
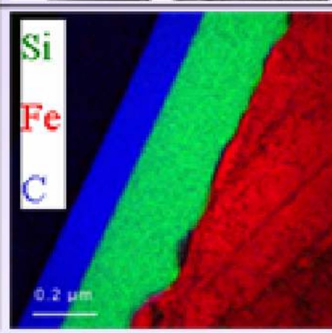


PMS in Acetylene

EFTEM zero loss image | EFTEM elemental map



Microstructure Summary

	PMS	PPS	PPMS	PPPS
Air				
Ar				
C_2H_2				

Summary

- Polysilsesquioxanes produce glassy Si-O-C films at 850˚C – 700˚C on metal substrates.
  - Ceramic yields are as high at 82% in Ar and N_2.
- Low-cost precursor to polysilsesquioxanes can be used to make cheaper coatings with more control over processing.
  - Current work with Yigal Blum of SRI.
- Preceramic polymer coatings produced from intermediate temperature pyrolysis of polysilsesquioxanes exhibit the following features:
  - In Ar observe Si-O-C glassy, adherent, brittle films. Some cracking observed for thicker films.
  - Pyrolysis performed in Ar showed little diffusion with exception of PPMS sample (Cr diffusion).
  - Pyrolysis performed in Air showed diffusion of Fe. Strong bonding.
  - Pyrolysis performed in Acetylene showed segregation of S and C regions within the coating but no diffusion of Fe or Cr.

Critical Issues

- Preceramic polymer coatings must be pyrolyzed at low temperatures ($T < 900°C$), exhibit insignificant cracking and/or porosity, match the CTE of metal substrate, and exhibit superior corrosion resistance.
- Coatings must be made from inexpensive starting materials and we have achieved that for the polymer precursor.
- Filler particles must provide proper shrinkage compensation and CTE match while maintaining corrosion resistance.
- Coating application technology must be made simple and industrially relevant (paint technology).

Future Goals

- Develop filled polymer coatings on steels with proper CTE match and corrosion resistance using inexpensive application technologies.
- Tailor polymer chemistry for low-temperature curing/pyrolysis with controlled amounts of carbon.
- Explore displacement reactions using Al to reduce SiO_2 to Si and undergo subsequent reactions.
- Measure film mechanical properties (UW task).
- Work with industrial partner to insure that coatings are tested and evaluated properly.